An Anatomy of Furnace Refractory Erosion:
Evidence from a Pilot-Scale Facility

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INTRODUCTION

Plasma-arc technology—and DC transferred-arc technology, in particular—has its adherents.[1,2] MINTEK is one of them. Since the late 1970s, it has sought to apply this technology to the recovery of valuable metals from certain ores and from furnace slags and dusts. Commercial furnaces are now in place for the production of ferrochromium from chromite and for the smelting of ilmenite. Beginning with small-scale DC-arc furnaces, it has demonstrated the application in four other areas:[2–7]

- The recovery of copper, nickel and cobalt from converter slags
- The recovery of nickel from nickel laterite
- The fuming of lead and zinc from lead blast-furnace slag (LBFS)
- The removal of zinc and lead from electric-arc furnace (EAF) dusts collected during steelmaking

Then, several years ago, the scale of work leapt with the commissioning of a 5.6 MVA (1–3 MW) facility. The furnaces, although larger (about 2.5 m in diameter), follow earlier designs—a cylindrical shell of water-cooled panels; a conical roof, through which the graphite cathode passes; and the facility to feed charge close to the arc. In most applications, an alumina castable protects the roof and an MgO rammable the hearth. The refractories of the sidewall, being the focus in this matter, vary according to the demands and concerns of each campaign. The right choice of refractory has always been integral to the success of a campaign. These days, the assessment of their performance provides invaluable pointers in choosing refractories for large-scale, industrial furnaces—it is for the purpose of designing these furnaces, after all, that campaigns on a pilot scale are conducted.

   The campaigns themselves have been good vehicles for testing refractories under particular conditions. One can cite two reasons:

1. Conditions in the small, pilot-scale furnace are sometimes more severe than those likely to be encountered in a industrial-scale furnace. The dimensions are such that, more than once, high temperatures have

prevented a freeze-lining from forming; and in at least one configuration, flaring from the arc impinged on a section of sidewall in the freeboard.

2. Severity notwithstanding, of all the tests one can devise, a campaign in a pilot-scale furnace best simulates the conditions that will prevail in an industrial furnace. Heat transfer profiles are similar, and both corrosive and erosive forces are at play:

   • The hot-face is at the refractory-slag interface and temperature drops across the refractory. This stands in contrast to the cup test, in which a crucible of the refractory, or a cavity drilled into a brick of the material, is filled with slag and heated in a furnace. This configuration forces temperature, when conditions have stabilized, to be uniform throughout the slag and refractory.
   • Continuous feeding and tapping keep the composition of slag in the bath constant. This maintains the chemical potentials driving corrosion. In the cup test, by contrast, the ratio of slag to refractory is low, with the effect that chemical potentials equalize when slag reacts with the refractory. The spindle test, in which a rotating rod of refractory is immersed in a bath of molten slag, would circumvent this flaw of the cup test if the bath were large in comparison with the immersed refractory.
   • Turbulence in the slag bath creates an erosive environment, one that a refractory must withstand.

These advantages, however, cannot offset the fact that tests in a pilot-scale furnace fail to give full and precise control over conditions at the slag-refractory interface. In a post-mortem examination, one is consequently unable to distinguish between, let alone measure, the interactive processes between slag and refractory—the very processes researchers consider to constitute corrosion and erosion. (This is a concern being addressed by a group at CSIRO Minerals, Australia. It has developed a gravimetric technique for providing "direct information" on the dynamic processes of wetting, penetration, dissolution and erosion of refractories by molten slags.[8]) We can, nonetheless, rank the performances of different refractories from similar campaigns; and, drawing on phase-chemical theory, we can interpret the clues offered by post-mortem examinations to identify the causes of erosion in a particular refractory. The details may not all be there, but an account of the broader mechanisms is.

A number of different refractories were used in several recent campaigns run in the 5.6 MVA, DC-arc furnace at MINTEK. This paper describes aspects of their corrosion and erosion. It offers explanations for what happened to them, and it draws some lessons regarding the choice of refractories in certain applications.

MATERIALS AND CONDITIONS

The campaigns involved the smelting of siliceous materials at conditions designed to minimize the reduction of iron from the slag in order to concentrate certain valuable metals. These metals can be recovered from any number of sources; this paper considers three:

• Nickel laterites
• Lead blast-furnace slags (LBFS)
• Copper reverberatory-furnace slags (CRFS)

The smelting of these materials produced slags of different composition (Table I). Comparing *just these* slags, one might highlight their relative qualities:

• A slag rich in magnesia and silica
• A slag rich in calcia and iron oxide
• A slag rich in calcia and silica. The alkali levels in this slag were also unusually high

The refractories were both shaped and unshaped (tables II and III).[9] Except for the silicon carbide bricks, they were all of the oxide variety. Two of the refractories—one a magnesia brick, the other a spinel castable—contained graphite. (They were chosen for their high thermal conductivity; although graphite does inhibit slag penetration, which increases resistance to spalling.[10]) Only sub-sets of the refractories were used in each campaign (Table IV). Several of them—the magnesia, magnesia-chrome, spinel, and silicon carbide refractories—were used in three or more campaigns.

Table I. Average Compositions of Slags Tapped from the Furnace in 7 Campaigns
(mass per cent)

	Ex Nickel Laterite		Ex Lead Blast-Furnace Slag		Ex Copper Reverberatory-Furnace Slag		
	1	2	1	2	1	2	3
CaO	0.3	0.3	20	23	20	19	13
MgO	32	35	2.5	5	4	3.5	4
FeO	16	13	39	36	17	17	20
Al_2O_3	2	5	5	4	9.5	9	9
Cr_2O_3	1.2	1.3	0.3	0.1	0.2	0.1	0.1
SiO_2	47	45	25	22	46	46	49
ZnO	. . . . .	. . . . .	4	4	. . . . .	. . . . .	. . . . .
$K_2O + Na_2O$	. . . . .	. . . . .	. . . . .	. . . . .	4	4	4

Principal Phases in the Cooled Slag

$(Mg,Fe)_2SiO_4$ (olivine)	$Ca_2(Mg,Fe,Al)(Si,Al)_2O_7$*	$Ca(Mg,Fe)(Si,Al)_2O_6$ (pyroxene I)
$(Mg,Fe)SiO_3$ (pyroxene)	$(Fe,Mg)O$ (magnesiowüstite)	$CaFe_{0.7}(Si,Al)_{2.3}O_6$ (pyroxene II)
	$Ca(Fe,Mg)SiO_4$ (kirschteinite)	$KAlSi_2O_6$ (leucite)

 * Akermanite, which formed in slag 2 with cooling. It was the dominant phase.

Table II. Compositions of Shaped Refractories: Chemical[†]
(mass per cent)

	Magnesia	Magnesia-Carbon	Magnesia-Chrome	Fused Spinel	SiC -Si_3N_4	SiC -SiO_2
MgO	96	87	59	28	. . . . .	. . . . .
Al_2O_3	0.3	9	7.5	72	0.3	0.7
Cr_2O_3	. . . . .	. . . . .	20	. . . . .	. . . . .	. . . . .
Fe_2O_3	0.3	0.5	10	0.1	0.3	0.7
SiO_2	0.8	2.3	1.6	0.1	0.5	8.5

Principal Phases (Approximate)

MgO (periclase)	96	74	48	. . . . .	. . . . .	. . . . .
$Mg(Cr,Fe,Al)_2O_4$ (chromite)	. . . . .	. . . . .	49	. . . . .	. . . . .	. . . . .
$MgAl_2O_4$ (spinel)	. . . . .	11	. . . . .	97	. . . . .	. . . . .
SiC	. . . . .	. . . . .	. . . . .	. . . . .	75	90
Si_3N_4	. . . . .	. . . . .	. . . . .	. . . . .	23	. . . . .
SiO_2 (cristobalite)	. . . . .	. . . . .	. . . . .	. . . . .	. . . . .	9
C (graphite)	. . . . .	15	. . . .	. . . . .	. . . . .	. . . . .

Physical Properties[†]

Bulk Density (g.cm^{-3})	2.87	2.80	3.23	2.94	2.65	2.55
Apparent Porosity (%)	18	10	16	17	17	18
Thermal Cond. (W.m^{-1}.K^{-1})*	4.1 (1000°C)	4.1 (1000°C)	2.6 (1000°C)	3.0 (1200°C)	16.3 (1480°C)	15.7 (1480°C)

 [†] From the manufacturers' data sheets.
 * Thermal conductivity of the refractory at the temperature reported in brackets.

Along with compositional differences in their slags, the campaigns differed in other respects. They did not all run for the same duration. Nine days was the norm, but two of the campaigns ran for much longer

periods (Table IV). Temperatures were also different (Figure 1). On the assumption that the temperature of tapped slag reflects the temperature within the furnace, we can see that the second campaign in the smelting of lead blast-furnace slag maintained relatively low temperatures (~1400°C); the second campaign in the smelting of nickel laterite, the hottest temperatures (~1700°C). The difference relates to the higher liquidus of the MgO-FeO-SiO_2 slag from nickel laterites compared with that of the CaO-FeO-SiO_2 slag from LBFS.[11, 12]

Table III. Compositions of Unshaped Refractories: Chemical
(mass per cent)

	Magnesia-Chrome	Alumina-Chrome	Alumina	Spinel	Spinel-Carbon
CaO	3	0.2	1.5	1.8	1.6
MgO	49	0.3	5	22	20
Al_2O_3	14	84	93	76	76
Cr_2O_3	18	10	. . . . .	. . . . .	. . . . .
Fe_2O_3	9	0.5	—	0.2	0.1
SiO_2	6	4	0.1	0.2	0.1
Principal Phases (Approximate)					
MgO (periclase)	30	. . . . .	. . . . .	. . . . .	. . . . .
(Mg,Fe)(Cr,Fe,Al)$_2$O$_4$ (chromite)	55	. . . . .	. . . . .	. . . . .	. . . . .
$MgAl_2O_4$ (spinel)	. . . . .	. . . . .	18	87	85
Al_2O_3 (corundum)	. . . . .	✓	75	10	10
$(Al,Cr)_2O_3$ (sesquioxide)	. . . . .	✓	. . . . .	. . . . .	. . . . .
$CaMgSiO_4$ (monticellite)	9	. . . . .	. . . . .	. . . . .	. . . . .
Mg_2SiO_4 (olivine)	6	. . . . .	. . . . .	. . . . .	. . . . .
CA_x (calcium aluminates)	. . . . .	. . . . .	✓	✓	✓
C (graphite)	. . . . .	. . . . .	. . . . .	. . . . .	2.5
Physical Properties					
Bulk Density (g.cm^{-3})	3.0	3.1	2.9	2.8	2.8

Past successes with certain refractories and a willingness to try new ones played a part in the choices of refractories made for the different campaigns. Physical factors were also considered. Any choice, however, should not fail to take cognizance of an important phase-chemical principle, that of the compatibility between slag and refractory. With thought given to it, the following precautions could be sounded:

- The slags, which are rich in FeO, will tend to oxidize a silicon carbide refractory and accelerate its erosion. Only a freeze lining will prevent this reaction. The choice of silicon carbide in three of the campaigns (Table IV) was prompted by a need for high thermal conductivities in order to establish a freeze lining.
- The slags will tend to oxidize the graphite in carbon-composite refractories, which will affect the wetting of the refractory and, therefore, slag penetration. Only a freeze lining will prevent this from happening.
- The slags, which contain little Al_2O_3, will tend to dissolve alumina refractories. Avoid these refractories unless a freeze lining is guaranteed.
- LBFS, which has relatively little silica, will dissolve silicate phases in those refractories that contain them. Choose refractories with little or no SiO_2.

The same phase-chemical principle, on the other hand, enables one to recommend that magnesia refractories be used in the smelting of nickel laterite, because the slag is rich in MgO.
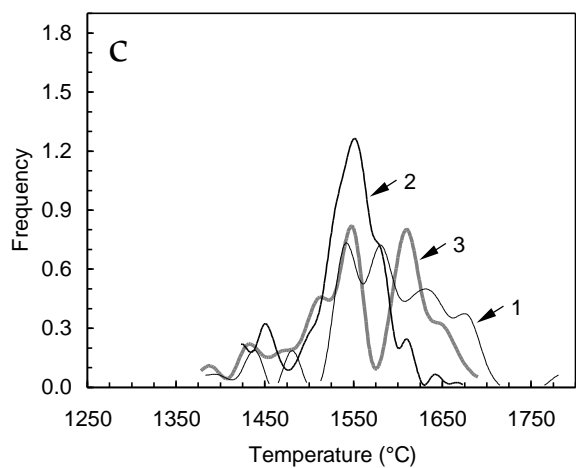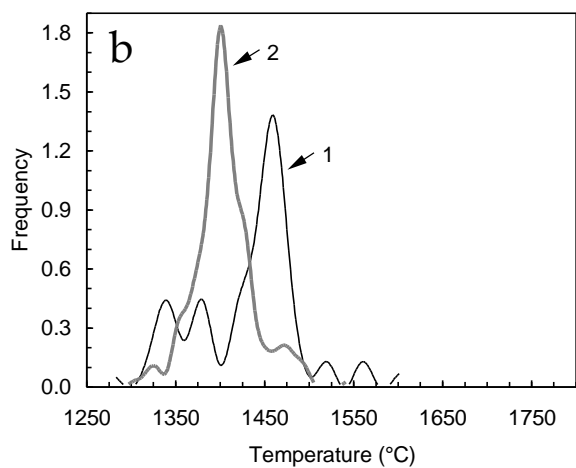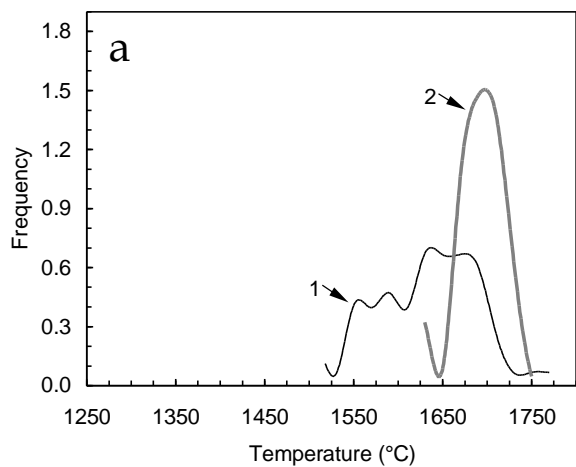
Figure 1. Temperatures of Tapped Slags
            (normalized variations in temperature).

   a. Smelting of nickel laterite.
   b. Smelting of lead blast-furnace slag.
   c. Smelting of Cu reverberatory-furnace slag.
The numbers refer to campaigns (see Table I).

Table IV. Combinations of Slags and Refractories: Shaped Refractories

	Ex Nickel Laterite		Ex Lead Blast-Furnace Slag		Ex Copper Reverberatory-Furnace Slag		
	1	2	1	2	1	2	3
Magnesia	✓	. . . .	. . . .	. . . .	. . . .	✓	✓
Magnesia-carbon	. . . .	. . . .	. . . .	. . . .	✓	. . . .	. . . .
Magnesia-chrome	✓	✓	✓	✓	. . . .	✓	. . . .
Spinel	. . . .	. . . .	. . . .	✓	✓	✓	✓
SiC Nitride bonded	. . . .	. . . .	. . . .	✓	. . . .	✓	✓
SiC Silicate bonded	. . . .	. . . .	. . . .	✓	. . . .	✓	✓
Unshaped Refractories							
Magnesia-chrome	. . . .	✓	. . . .	. . . .	. . . .	. . . .	. . . .
Alumina-chrome	. . . .	. . . .	✓	. . . .	. . . .	. . . .	. . . .
Alumina	. . . .	. . . .	. . . .	. . . .	✓	. . . .	. . . .
Spinel	. . . .	. . . .	. . . .	. . . .	✓	. . . .	. . . .
Spinel-carbon	. . . .	. . . .	. . . .	. . . .	✓	. . . .	. . . .
Campaign Duration (days)	9	10	9	18	9	25	9

REACTIONS, RESISTANCE AND FAILURES

In all seven campaigns, corrosion was the cause of failure in many of the refractories lining the sidewall of the furnace. It manifested itself in two ways:

1. As a dissolution reaction *at* the hot-face. The driving force in this process is the lower activity of the refractory-oxide component—*i.e.,* MgO, Al_2O_3 or Cr_2O_3—in the slag. (A similar imbalance drives FeO into the refractory.) In a closed system, the dissolution process would continue until the slag reached saturation. In practice, however, because the slag composition is held constant, the point of saturation is never reached and dissolution continues until the entire refractory is consumed.
2. As a loss of refractoriness *behind* the hot-face. Here, slag penetrates the refractory. The introduction of CaO, FeO and SiO_2 lowers the solidus temperature of the refractory to well below the prevailing temperature. The consequence is a turning of part of the refractory to liquid. This weakens the refractory, making it susceptible to any turbulence in the slag or metal bath. As these currents impinge on the lining, so the refractory succumbs to erosion.

Several local factors would determine which of these mechanisms prevailed at any point in the furnace or in any refractory. Structural characteristics (*i.e.,* the porosity and grain-size distribution of a refractory) and interfacial properties (*i.e.,* the surface tension between a given slag and refractory, which influences wetting) determine the extent to which a slag will penetrate a refractory. On the other hand, high temperatures in the furnace and sharp gradients in the refractory lining would tend to favour reactions at the hot-face over those behind it. Without our having measured the physical properties directly, we can only *infer* their likely effects from a post-mortem examination of the refractories in the light of generally understood principles, or remain silent.

$MgAl_2O_4$ (Spinel) in Contact with CRFS

We can represent this combination by compositions within the system $CaO-MgO-Al_2O_3-SiO_2$. (The system accounts for the principal species in the slag at and behind the hot-face. We can ignore FeO on the grounds that Fe^{2+} will diffuse into the grains of spinel, which accommodates it in solid solution. This, indeed, is what happened.) Phase relations at liquidus temperatures in the system have been published for planes of constant Al_2O_3.[11, 12] The composition of CRFS can be represented on the diagram cutting the 10% Al_2O_3 plane of the system (10% approximates the alumina content of the slag—Table I). It lies over the pyroxene primary-phase field. At 1550–1600°C, therefore, the slag is not in equilibrium with $MgAl_2O_4$ (spinel); being unsaturated with

MgO and Al_2O_3, it will dissolve the refractory until it is in equilibrium with $MgAl_2O_4$. The dissolution process can be tracked through the system across planes of increasing Al_2O_3: at 15% Al_2O_3, the spinel primary-phase field has appeared and begun expanding; at 25% Al_2O_3, the slag composition has begun to move over the spinel field; between 30 and 35% Al_2O_3, it moves across the 1550–1600°C isotherms. Only when the point representing the slag composition falls within the spinel primary-phase field and converges with the isotherm representing the bath temperature does further dissolution of spinel from the refractory cease. The point of saturation is reached when the Al_2O_3 fraction in the slag has risen to between 30 and 35%; in the process, the slag will have consumed 45–65% of its mass in $MgAl_2O_4$ (spinel). Without a freeze lining, therefore, one can expect CRFS to do considerable damage to spinel refractories.

That the bricks of fused spinel sustained severe erosion is a clear indication that a freeze lining was not maintained at the base of the furnace (Figure 2a). Further up the sidewall, cooling panels held down temperatures in the lining sufficiently for corrosion and erosion to have been minimal (Figure 2b). The microscopic evidence points to a dissolution of $MgAl_2O_4$ (spinel) at the hot-face as the mechanism of erosion:

- As Figure 3 strikingly shows, the slag-refractory interface 'slices through' $MgAl_2O_4$ (spinel) grains at the eroded face of the fused-spinel brick; the interface is sharp and smooth over the full surface of the hot-face. No loose grains of spinel lay in the layer of slag adhering to the hot-face, a sign that the refractory had not first been weakened by corrosion and then washed by currents into the bath.
- Slag penetrates the matrix in both brick and castable. Within the pores, its composition is enriched in Al_2O_3. Analyses of the slag phase trace a sharp increase in the level of Al_2O_3 from a point at the hot-face (~10%) to one just behind it (>25%). There was no evidence that the reaction of slag with $MgAl_2O_4$ (spinel) in the pores of the refractory contributed to erosion.
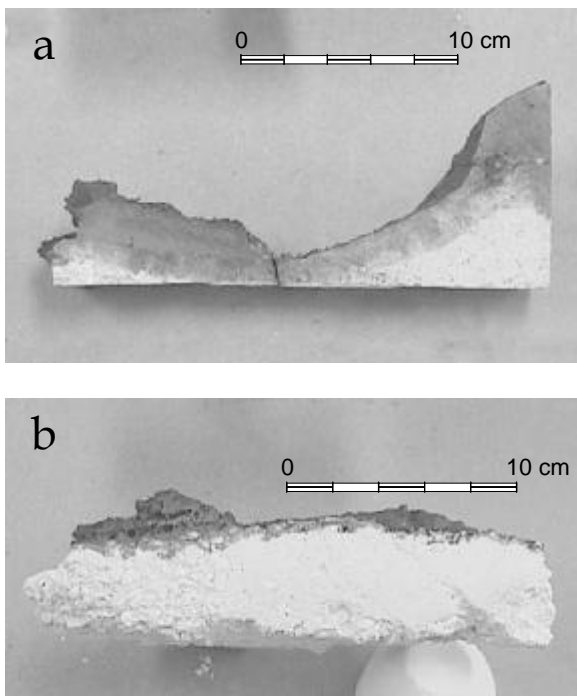

Figure 2. Corrosion/Erosion of Spinel
　　　　　Refractories in Contact with CRFS.
　a. Brick of fused spinel from base of furnace.
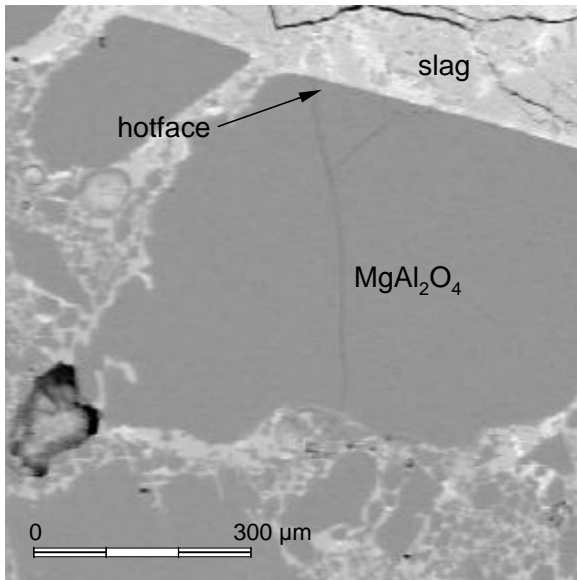　**b.** Castable against cooling panel.

Figure 3. Refractory-Slag Interactions at the Hotface of a Spinel Brick. Micrograph of the backscattered-electron image.

Magnesia-Chrome in Contact with LBFS

In theory, one can represent this combination by compositions in the system CaO-MgO-FeO-Cr_2O_3-SiO_2. In practice, however, given the constraints of presenting phase diagrams in two dimensions and omissions in the corpus of published diagrams, such a representation is no easy task. The composition of the slag maps conveniently onto the phase diagram for the system CaO-iron oxide-SiO_2 in contact with metallic iron.[11, 12] Introducing MgO (periclase) and $Mg(Cr,Fe,Al)_2O_4$ (chromite)—phases making up the refractory—complicates matters immeasurably. A simpler tack is desirable. The marked difference in compositions of the slag and refractory suggests that the two might be incompatible. Whereas the refractory contains about 60% MgO (Table II), the slag contains no more than 5% MgO (Table I). The considerable disparity in these numbers make it very likely indeed that LBFS, in contact with a magnesia-chrome refractory, is unsaturated with MgO. (Despite similar differences in Cr_2O_3, the chrome solubility in such FeO-rich slag—by implication, fairly oxidizing—would be low.) The evidence of microscopy and energy dispersive spectrometry (EDS) supports this conclusion:

- The hot-face defines a sharp boundary between the refractory and the slag of the bath (Figure 4). We would interpret this feature as erosion by dissolution.
- Not only is the cooled slag adjacent to the hot-face enriched in Mg^{2+}, but, where it has been left relatively undisturbed, a spinel rich in magnesia and chrome has crystallized from the molten slag. This phase and its chrome-magnesia-rich composition indicate that the slag in this area, shielded from turbulence in the slag bath, had reached saturation, the outcome of a dissolution process.

Not surprisingly, without a freeze-lining to protect them, the magnesia-chrome bricks that contained the slag bath were severely eroded in the shorter campaign and entirely consumed within 18 days (Table IV). Erosion was just as severe in magnesia-chrome refractories lining the lower sections of the freeboard.
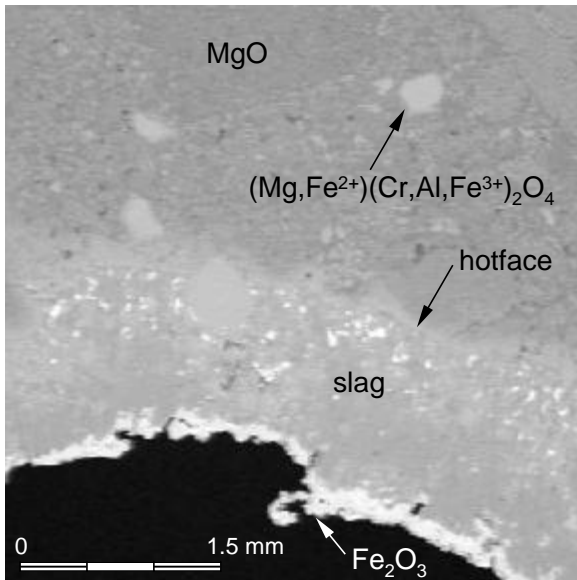
Figure 4. Refractory-Slag Interactions at the
Hotface of a Magnesia-Chrome Brick.
Micrograph of the backscattered-electron image.

Magnesia, Mag-Chrome and Ni Laterite Slags

Considering the high level of MgO in the slag (Table I), one would be prudent in lining the furnace with a magnesia refractory. The evidence seems to bear out the validity of this line of reasoning. Not that erosion did not occur; rather, bricks of magnesia in the samples we collected sustained less erosion over the hot-face in contact with the slag bath than those of magnesia-chrome (*cf*. figures 5 and 6. The localized erosion coincident with the metal-slag interface—grooves marked X—is a manifestation of the Marangoni effect[13, 14]). We can explain the difference with reference to the appropriate phase diagrams. The combination of a magnesia refractory in contact with a slag produced in the smelting of nickel laterite can be represented by the system MgO-SiO_2. As in a previously discussed combination, we can ignore FeO on the grounds that Fe^{2+} diffuses into MgO (periclase), which accommodates it in solid solution. We found phases of the slag in close proximity to grains of MgO to contain far less FeO than the bulk slag; the grains themselves had become (Mg,Fe)O (magnesiowüstite). Looking at the phase diagram for the system MgO-SiO_2, one can see that points representing the slag—compositions between 55 and 60% SiO_2 at temperatures between 1600 and 1700°C—lie within the liquid field close to the Mg_2SiO_4 (olivine) liquidus.[11, 12] As Mg_2SiO_4 (olivine) co-exists with MgO (periclase) at these temperatures, we can conclude that the slag is just short of being saturated with MgO. The driving force in dissolution—corresponding to the displacement between the compositions of the slag and liquidus on the phase diagram—would be relatively small.

For a magnesia-chrome refractory, by contrast, this driving force is much greater. Here, though, the exercise is complicated by more components in the system to be considered. There is as yet no complete phase diagram for system MgO-FeO-Cr_2O_3-Al_2O_3-SiO_2 in equilibrium with metallic iron. The phase diagrams to four sub-systems, however, give some indication of what one can expect to find in the larger system. The four are—[11, 12]

- MgO-Cr_2O_3-SiO_2 in equilibrium with air
- MgO-Cr_2O_3-SiO_2 in equilibrium with metallic chromium
- MgO-Al_2O_3-SiO_2
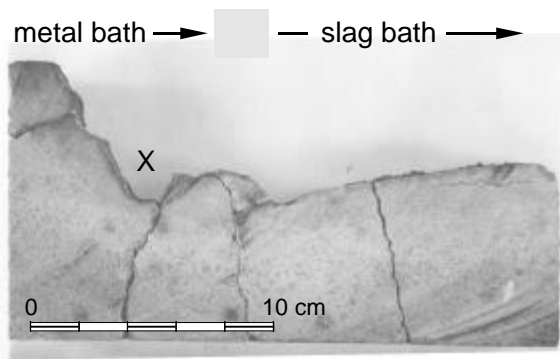- FeO-Al_2O_3-SiO_2 in equilibrium with metallic iron

Figure 5. Erosion of a Magnesia Brick in the
Smelting of Nickel Laterite.
X marks the eroded groove formed at the slag-
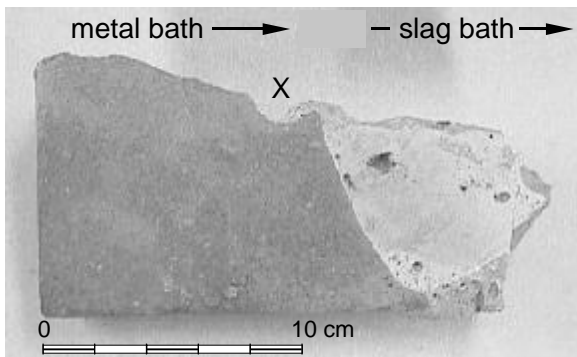metal interface.

Figure 6. Erosion of a Magnesia-Chrome Brick
in the Smelting of Nickel Laterite.
X marks the eroded groove formed at the slag-
metal interface.

At 1700°C, the liquid field covers a very small area of the system MgO-Cr_2O_3-SiO_2 in equilibrium with air. It expands across the phase diagram when the system is in equilibrium with metallic chromium.[12] Because metallic iron imposes a less reducing potential than does metallic chromium, we can expect the liquid field to cover an area of intermediate extent when the system MgO-Cr_2O_3-SiO_2 is in equilibrium with metallic iron. Phase relations in the second and third phase diagrams would suggest that, with the introduction of Al_2O_3 and FeO into the system, the liquid field expands in other directions. The slag composition falls within this field; it also lies within the confines of the olivine primary-phase field, possibly close to the olivine liquidus. The slag composition is at some remove from the spinel liquidus, however. One can follow the implication of this geometry with the introduction of a magnesia-chrome refractory into the picture. The refractory is a composite of MgO (periclase) and $Mg(Cr,Fe,Al)_2O_4$ (chromite; see Table II). In contact with MgO (periclase), the slag should be slightly unsaturated with MgO; in contact with $Mg(Cr,Fe,Al)_2O_4$ (chromite), it should be unsaturated with Cr_2O_3 and Al_2O_3 by a considerable margin. Cr_2O_3 and Al_2O_3 will dissolve into the slag. This would explain the erosion of magnesia-chrome refractories during the campaign.

Quite how active the dissolution process is, is suggested by the sharp divide between slag and refractory at the hot-face (Figure 7). The presence of pores immediately behind the hot-face suggests that the penetration

of slag into the refractory is minimal, if not marginal. The mechanism of erosion, therefore, was by the dissolution of refractory *at* the hot-face, and not by any corrosion and disintegration of the refractory behind it (although this does seem to have been the mechanism of erosion at the slag-metal interface).
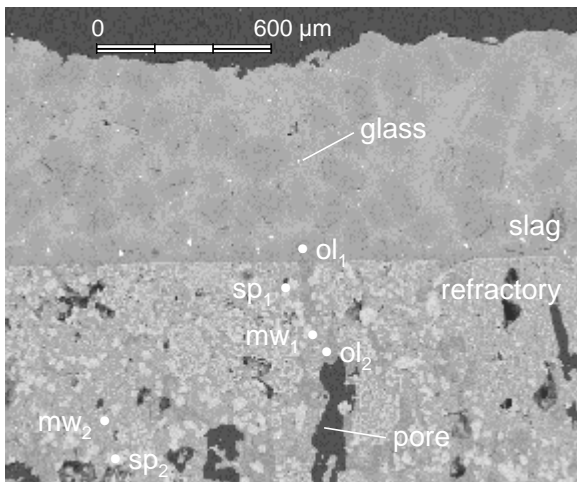

Figure 7. A Chromite Aggregate at the Hot-Face of a Magnesia-Chrome Brick (Nickel Laterite Smelting).
Micrograph of the backscattered-electron image.

LEGEND

ol_1	$Mg_{1.9}Fe_{0.1}Si_{1.0}O_4$
ol_2	$Mg_{1.9}Fe_{0.1}Si_{1.0}O_4$
sp_1	$Mg_{0.9}Fe_{0.1}(Cr_{1.1}Al_{0.9})O_4$
mw_1	$Mg_{0.86}Fe_{0.10}Cr_{0.02}O$
sp_2	$Mg_{0.9}Fe_{0.1}(Cr_{1.0}Al_{0.9}Fe_{0.1})O_4$
mw_2	$Mg_{0.87}Fe_{0.09}Cr_{0.02}O$

While the magnesia-chrome brick displayed a consistent pattern of erosion, slag-refractory interactions in the magnesia-chrome castable varied. This variation reveals something of the effect that different conditions had on the erosion process, because, unlike the bricks, the castable spanned much of the height of the sidewall, and local conditions varied up the wall. We identified three contexts:

- *Against the cooling panel in contact with the slag pool.* Slag had penetrated the refractory and brought on the disintegration of the hot-face, which consequently lacked definition.
- *Against the cooling panel in the freeboard.* There is some penetration of slag into the refractory, but the refractory retains a sharp edge with the slag.
- *Above the cooling panel in the freeboard.* The slag adhering to the hot-face is layered, and the hot-face, following its disintegration by slag, lacks definition.

In all three instances, slag had penetrated the refractory. We would surmise that the porosity of the castable and the Ca, Mg silicates in its matrix facilitated this penetration. But, given that all internal factors would have been equal in each instance, the process of erosion had to have been controlled by one or more external factors. We know that at least one condition varied up the sidewall, namely, the thermal history of the hot-face at each location. The factors at play here are the impositions of temperature from the bath or the freeboard and the forced cooling imposed on the refractory by the cooling panel. The likely combination of their effects seems to be consistent with our observations. The second context combined the forced cooling of the panel with the cooler, more stable environment of the freeboard. Along with forcing *down* the temperature of the hot-face, the

combination would have imposed a *steadier* temperature on the hot-face. The effect would have minimized slag penetration and the attendant disintegration of refractory behind the hot-face; the hot-face itself would have receded (through dissolution) until its temperature matched the liquidus of the slag. In the first and third contexts, the hot-face of the castable would either have been subjected to greater fluctuations in temperatures, or not have had the benefit of forced cooling. The slag in the pores would have set up a zone of disintegration that marks the hot-face as indistinct.

Alumina, Alumina-Chrome and LBFS or CRFS

The two combinations are an alumina castable in contact with CRFS and an alumina-chrome rammable in contact with LBFS (tables II and III). The castable contained over 98% Al_2O_3 + MgO; the rammable, ~4% SiO_2. Both refractories lined the sidewall against the slag bath and the freeboard, and both shielded cooling panels.

The project investigators installed these refractories with different purposes in mind. Their intention was for nothing of the alumina-chrome rammable to remain, which is what happened, save for small fragments isolated in a corner of the lining. The alumina refractory was meant to survive, which it did: ~3 cm of the lining remained against the panels. Sections through samples of the alumina castable revealed the slag to have penetrated ~1 cm of the refractory. On the other hand, a section through the alumina-chrome fragment revealed little penetration—indeed, the slag encountered the refractory at a fairly sharp interface; the hot-face was well-defined across matrix and aggregates.

How do these results square with phase-chemical theory? Both refractories, being essentially alumina, would have been incompatible with either slag, which contain less than 10% Al_2O_3. The unsaturated slag would have dissolved Al_2O_3 from the refractories. The alumina-chrome refractory would have been further disadvantaged by Cr_2O_3 and SiO_2. That the alumina castable survived as it did, even that a fragment of alumina-chrome refractory survived, attests to the efficacy of the cooling panels, if not the properties of the refractories. The fragment of alumina-chrome refractory was particularly revealing. Over much of the sidewall, its chemical composition, along with the control of energy flux through the wall, allowed slag to erode the refractory; yet in the fragment, there was little penetration of the matrix by slag and no sign of any weakening of refractory behind the hot-face. Erosion occurred by the dissolution of refractory at the hot-face. Because the fragment survived, we would surmise that the lining in that vicinity probably benefited from better cooling and less turbulence.

Silicon Carbide and LBFS or CRFS

Nitride-bonded silicon carbide (SiC-Si_3N_4) lined the sidewall in contact with the slag bath of three campaigns. Investigators reasoned that the high thermal conductivity of the refractory (see Table II) would make it easier to establish a freeze lining, and so preserve the refractory. The unexpected happened, however. Whereas the lining survived largely intact after 25 days of smelting CRFS at ~1550°C, it disappeared after 18 days of smelting LBFS at ~1400°C. Clearly, for a time at least, a freeze lining did not exist. It was only after investigators pointed out measures taken to prepare the lining for the LBFS campaign that we could make sense of this result. We now believe the destruction of the SiC lining in that campaign to have been initiated during a 36 hour period prior to commencement. Because the bricks did not fit tightly together, the gaps between them were filled with a SiC mortar, which required curing. Burners were lit. They would have oxidized SiC to SiO_2, which would subsequently have dissolved readily in slag. The lining would have eroded fairly quickly.

Had this not happened, however, the refractory would still have faced another destructive process—albeit a far milder one. The evidence appeared in a sample from the CRFS campaign. Close examination of refractory near the hot-face identified three features not present in the virgin refractory:

• Specs of carbon in the matrix of the refractory.
• A layer of silica (SiO_2) on the surfaces of many particles of SiC (Figure 8). This would suggest that conditions in the furnace were sufficiently oxidizing for SiO_2 to form from SiC.

- An alloy phase containing high levels of silicon (Figure 9—an analysis of the alloy at one point recorded 15% Si).
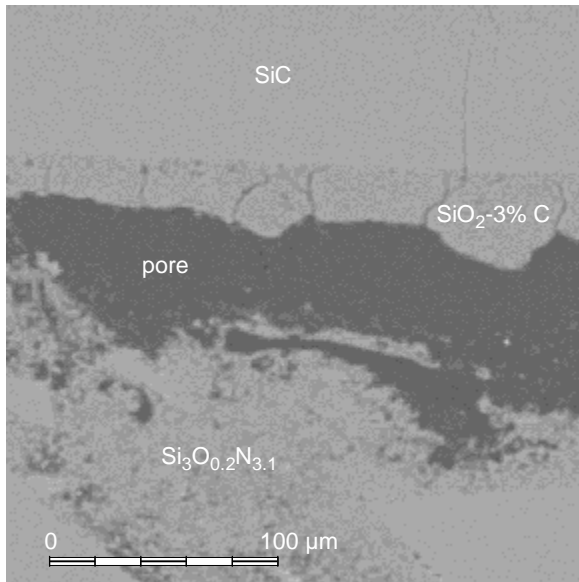

Figure 8. Near the Hot-Face of SiC-Si_3N_4
　　　　　Refractory: Formation of SiO_2.

Micrograph of the backscattered-electron image.

To explain these features, we refer to the oxygen potentials of several buffers (Figure 10). Each of the shaded discs represents a set of desirable operating conditions for a campaign. Here, desirable refers to the minimal reduction of iron from the slag so that the liquid alloy will concentrate the valuable metals. The equilibrium curves for these metals lie above the shaded discs, which in turn lie close to the Fe^0-FeO buffer. These operating conditions will oxidize SiC to SiO_2: the reaction is driven by an oxygen potential of ~8 log pO_2 units, the difference in oxygen fugacities of the shaded discs and the SiC-SiO_2 buffer. Within the lining, the presence of SiO_2 and SiC will establish a local oxygen fugacity according to the SiC-SiO_2 buffer curve. In practice, by virtue of its proximity to the Si-SiO_2 buffer—less than 2 log pO_2 units separate the two buffer curves—this pO_2 is sufficiently reducing for the formation of a dilute, Si-bearing alloy. Thus, conditions near the hot-face of a SiC refractory stabilize SiO_2 and silicon. SiO_2, being soluble in slag, will facilitate the erosion of the lining. Silicon, on the other hand, should report to the liquid alloy. This, indeed, is what happened.
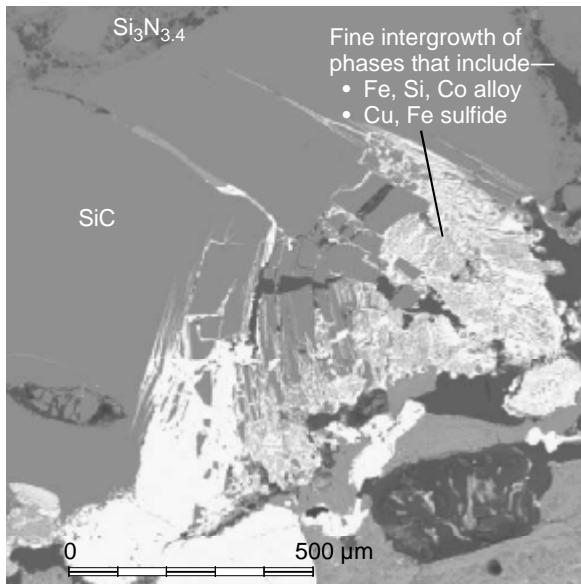
Figure 9. Near the Hot-Face of SiC-Si$_3$N$_4$ Refractory: Si-Enriched Metal.

Micrograph of the backscattered-electron image.

Graphite in Refractories

Oxygen fugacities in CRFS also played a role in the performances of the two refractories that contained carbon. The two were installed for their thermal conductivities, the spinel-carbon castable in the sidewall in contact with the slag bath. After the campaign, it was found to be covered by a plate of metal; the plate took the uneven form of liquid iron running down the sidewall. The refractory behind the hot-face was marked by the absence of graphite flakes; slag had penetrated the pores. There can be little doubt that graphite in the refractory reduced some of the considerable FeO in the slag. Liquid metal precipitated against the hot-face, while the loss of carbon opened up pores to the infiltration of slag. The formation of metal could have had a beneficial consequence, however: as the metal formed against the hot-face, it could have shielded the refractory from the corrosive effects of the slag bath. On the whole, the erosion of this refractory was not noticeably worse than its non-carbon counterpart.
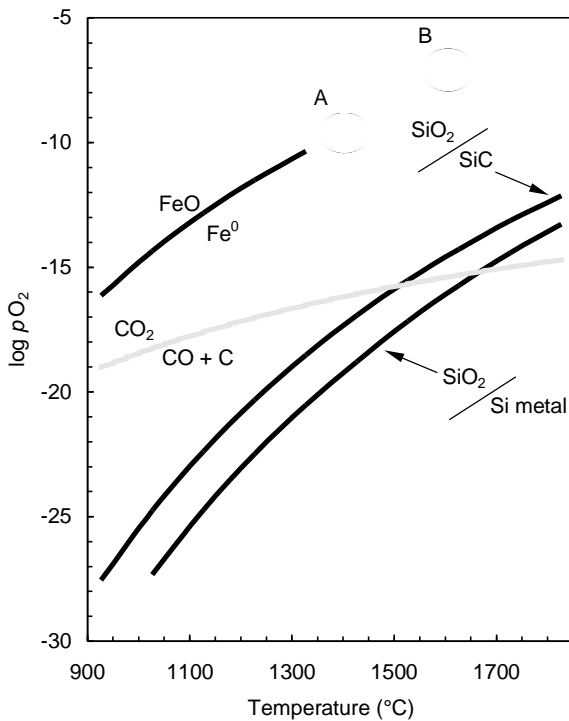
Figure 10. Oxygen Potential Diagram: Relative Stabilities of Different Buffers.

(Constructed from thermochemical data.[15]) The two shaded discs mark desirable operating conditions—

  A For the smelting of LBFS.
  B For the smelting of CRFS.

At these conditions, the reduction of Fe^{2+} to metallic iron should be minimal.

The magnesia-carbon bricks were never meant to come into contact with either molten slag or liquid metal; they were shielded by an inner course of refractories. But the latter suffered excessive erosion, which exposed some surface of the magnesia-carbon bricks to the bath. Erosion was severe.

Spinel Refractories in the Freeboard

In several of the campaigns, investigators favoured spinel refractories in the sidewall of the freeboard. Bricks were preferred to castables; only in one of the earlier campaigns did a furnace run with a castable lining. It spalled severely. In casting about for an explanation, we ruled out stress caused by a possible volume change in firing. The change in refractory volume was negligible.

Firing—or rather the lack of it—seemed have been the critical factor in spalling. The manufacturer of the spinel castable stipulated a programme of drying followed by firing. All that the castable in the furnace got was a partial curing at 400°C (higher temperatures would have damaged the cooling panels behind the refractory lining). Laboratory tests on pressed pellets of the castable demonstrated that firing at 1400°C (as stipulated) gave the refractory a strength that was wholly lacking in the material cured at 400°C. The lining, therefore, was inadequately prepared for the rigour of a smelting campaign.

That said, however, a brick of fused-spinel from the freeboard of the second LBFS campaign showed spalling (Figure 11). Although slag temperatures in the bath were much cooler (*cf*. figures 1b and 1c), the

electrode configuration raised the level of arc flaring in the freeboard. But if flaring were the sole cause, then the magnesia-chrome refractories in the freeboard should also have shown signs of spalling, which they did not. Spinel refractories, it seems, are particularly susceptible to spalling when attacked by slags, castables more so than fused-spinel. Conditions such as arc flaring may exacerbate matters.
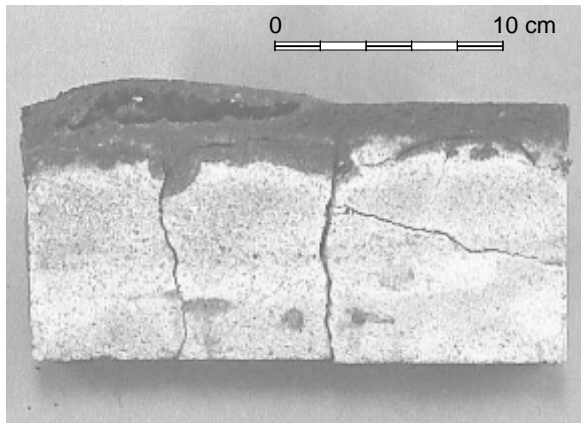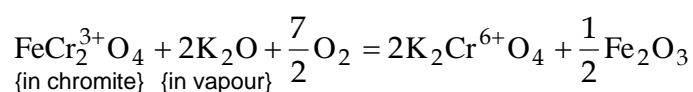

Figure 11. Spalling at the Hotface of a Fused-
Spinel Brick from the Freeboard.

Cr-bearing Refractories and CRFS

For the second campaign in the smelting of CRFS, magnesia-chrome bricks were installed in the sidewall of the furnace. Those lining the freeboard fared well. Samples were collected and sectioned for examination. Soon after they were cut, however, a bright yellow salt began appearing on their surfaces (but not on the hot-face or the compact zone immediately behind it). Powder X-ray diffractometry identified a mixture of $K_3NaCr_2O_8$ and K_2CrO_4 (tarapacaite). Both are salts of chromium(VI). Their appearance followed the use of water during cutting: it dissolved and mobilized the Cr(VI) salts, which then crystallized on the surface.

The formation of Cr(VI) salts recalls the alkali roasting of chromite ores. In that process, chromite is roasted with sodium carbonate in air at 1100–1150°C to convert trivalent chromium to its hexavalent form.[16] A similar reaction took place in the magnesia-chrome refractories of the freeboard. The key agents were potassium and sodium: the fumes from the bath contained almost 15% K_2O (*cf.* Table I). These alkalis, along with enough oxygen in the freeboard of the furnace, would have initiated the following reaction:

$$\underset{\{\text{in chromite}\}}{FeCr_2^{3+}O_4} + \underset{\{\text{in vapour}\}}{2K_2O} + \frac{7}{2}O_2 = 2K_2Cr^{6+}O_4 + \frac{1}{2}Fe_2O_3$$

It is significant that Cr(VI) salts formed only in the magnesia-chrome refractories of the freeboard; the sectioned magnesia-chrome bricks from the slag-metal line were devoid of yellow crystals. Beneath the surface of the slag pool, conditions would have been too reducing for the formation of alkali chromates(VI).

The threat Cr(VI) poses to health compelled investigators to ban chrome-based refractories from further campaigns to smelt CRFS. In the smelting of nickel laterites and LBFS, however, none of the chrome-bearing refractories showed any discernable Cr(VI).

CONCLUSIONS AND LESSONS

The 5.6 MVA, DC-arc furnace at MINTEK has proved itself an invaluable facility for testing refractories in contact with slags under the harshest of smelting conditions. Unlike the practice in industry, where furnaces run

with a freeze lining, there were times when the pilot-scale tests described in this paper did not run with one. We were able, therefore, to see how well refractories survived in direct contact with molten slag over a number of days. Our examinations of the phases in and morphologies of reaction zones, interpreted in the light of appropriate phase-chemical theory, provided a means for explaining what happened. Our observations lead us to conclude that—

- The dissolution of refractory *at* the hot-face is the principal mechanism by which oxide refractories submerged in a slag bath are eroded. This holds for the smelting of nickel laterite, lead blast-furnace slag and copper reverberatory-furnace slag. The mechanism appears to outweigh any loss of refractoriness *behind* the hot-face. There are even indications that differences in structural or physical properties matter little.

- Dissolution is driven by the low chemical potentials of one or more of the refractory oxides in the slags; being unsaturated with MgO, Al_2O_3, or Cr_2O_3, the slags dissolve these oxides from the refractories.

- In fused-spinel bricks in contact with CRFS and magnesia-chrome bricks in contact with either LBFS or slag from nickel laterite, erosion is severe. Magnesia bricks appear to offer better resistance to slags from the smelting of nickel laterites—which are rich in MgO—than do magnesia-chrome bricks.

- Even if a proper freeze lining is not established, cooling panels in the sidewall can be effective in halting the erosion of refractory linings.

- Siliceous slags rich in FeO are potentially destructive towards SiC refractories. They oxidize SiC to SiO_2, which either dissolves in slag, thereby facilitating the erosion of the refractory, or establishes an equilibrium with silicon, which reports to the metal as a contaminant. The formation of SiO_2 may also change the thermal conductivity of the refractory enough to destabilize a freeze lining.

- Slags rich in FeO are potentially destructive towards carbon/graphite in refractories. Carbon reduces FeO and certain other oxides to metal. Without graphite protecting them, these refractories are more susceptible to the corrosive effects of slag.

- Unshaped refractories must be properly cured. If this cannot be done, find an alternative.

- Spinel refractories lining the freeboard tend to spall. Castables may do so more readily than bricks of fused spinel.

- CRFS produces Cr(VI) in chrome-bearing refractories lining the freeboard. Keep such refractories away from any furnace smelting slags with even a few per cent K_2O or Na_2O.

ACKNOWLEDGEMENTS

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